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January 29, 1952

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ABSTRACT

The nuclear gyromagnetic ratio of vanadium 50 was determined in a nuclear induction spectrometer. An electronically regulated electromagnet maintained a field homogeneous to 0.1 gauss over the sample volume. Frequency measurements were made using a BC-221 frequency meter with an external 100 kc crystal-controlled oscillator and checked against radio station WWV (10 mc). The sample consisted of 271 mg of vanadium as vanadium oxytrichloride ($VOCl_3$) of which about 10 per cent was V50. This was prepared from enriched vanadium pentoxide (V_2O_5) by a standard chemical vacuum technique. Measurements at three values of magnetic field gave the following ratio:

$$\nu(V50)/\nu(D) = +\ 0.649527 \pm 0.00007\ .$$

The sign of the moment was determined to be positive by comparison with Rb85 and C135. Using the value of 2.7926 nuclear magnetons (n. m.) for the proton moment and Levinthal's deuteron-to-proton ratio of 0.1535059, the nuclear gyromagnetic ratio for V50 becomes + 0.55690 ± 0.00006.

New frequency ratios for V50/Rb85, V50/C135, Rb85/C135, Rb85/H1, and C135/H1 are included and compared with previously reported values.

THE NUCLEAR GYROMAGNETIC RATIO OF V50 AND MEASUREMENTS ON Rb85 AND Cl35

INTRODUCTION

The existence and natural abundance of vanadium 50 were announced by Leland[1] in 1949 and various measurements of its abundance have been made by others.[2] These measurements range from 0.23 per cent to 0.28 per cent. Recently,[3] a few milligrams of the isotope were electromagnetically enriched in the calutron and it was decided to search for the nuclear resonance signal in this material. The nuclear induction measurements are described later.

Normal $VOCl_3$[4] was tested for the known V51 signal and found to yield a very strong signal without the addition of a magnetic catalyst. Because of the difficulty of handling $VOCl_3$, which is very corrosive and volatile, several other compounds were tested. The results of these tests indicated that the V51 signal from $VOCl_3$ was many times larger than that of the other compounds checked and it was decided to convert all the available enriched V_2O_5 to $VOCl_3$.

THE PREPARATION OF $VOCl_3$ FROM V_2O_5 ENRICHED IN V50

Archibald[5] describes the preparation of pure $VOCl_3$ as worked out by Briscoe and Little.[6] He also refers to the previous work of Meyer and Backa,[7] Meyer and Markowicz,[8] and also that of Stahler and Wirthwein.[9] The original work was due to Berzelius.[10] The reactions are as follows:

$$V_2O_5 + 2H_2 = V_2O_3 + 2H_2O$$

$$3V_2O_3 + 6Cl_2 = 4VOCl_3 + V_2O_5$$

It is seen that only two-thirds of the vanadium is converted from V_2O_5 to $VOCl_3$ in one pass on this series of reactions. Thus, three conversions were performed in order to convert as much of the vanadium to $VOCl_3$ as was believed necessary. There was 526.4 mg of enriched V_2O_5 available,

and a total of 484.2 mg V_2O_5 (92 per cent) was converted to $VOCl_3$ in three conversions. The enriched $VOCl_3$ was collected in break-seals in vacuo (Fig. 1). The three break-seals with strikers were then attached to a header (Fig. 2) and all of the enriched material transferred in vacuo to a glass bubble of approximately 0.5 cc volume and the bubble sealed off. The bubble was then put into a larger tube (Fig. 3) and normal $VOCl_3$ was made as before and collected around the bubble which floated in the liquid. This was done in order to get as much of the V50 isotope as possible into the space available in the nuclear induction apparatus because the signal was expected to be very weak. When the signal was found with this "compound sample," it was observed to be unexpectedly strong. The glass bubble of enriched $VOCl_3$ was therefore removed from the normal material and transferred to a test tube containing a saturated aqueous solution of rubidium chloride (RbCl). Frequency comparisons were then made with Cl35 and Rb85 as described later.

The vacuum techniques used are similar to those described by Calvin[11] and collaborators. The enriched conversion procedure was as follows: The apparatus was assembled as shown in Fig. 1, evacuated and tested for leaks, then let down to air. A stream of purified hydrogen was passed over the V_2O_5 at 525°C for three hours. The hydrogen from a cylinder was bubbled through concentrated sulfuric acid (H_2SO_4), passed through pellets of potassium hydroxide (KOH) and then over copper turnings heated to 350°C and finally over phosphoric pentoxide (P_2O_5). After reduction to vanadium trioxide (V_2O_3) was completed, it was allowed to cool, the gas flow was cut off, and the system evacuated and torched so as to remove all traces of water from the reduction process. The system was then let down to atmospheric pressure with chlorine which was dried by bubbling through concentrated H_2SO_4 and over P_2O_5. A -30°C trap was applied (dibutyl carbitol and dry ice) and the V_2O_3 heated to 350°C in a flow of chlorine. The reaction proceeded rapidly and $VOCl_3$ distilled over into the trap; after the reaction was complete, the excess chlorine was flushed out with dry nitrogen, the trap was cooled to -65°C and the system evacuated. The system was then isolated by sealing off at the constrictions and the $VOCl_3$ distilled into the break-seals in vacuo using a liquid nitrogen trap to cool the break-seal. Finally the break-seal was sealed off.

The normal conversion was run similarly except that no cold traps were used, and the $VOCl_3$ was collected at room temperature. The tube was sealed off at atmospheric pressure of chlorine.

The combination procedure was merely a vacuum transfer accomplished by using glass-enclosed metal strikers to break the break-seals. The enriched $VOCl_3$ was collected in the small (0.5 cc) glass bulb and sealed off under vacuum.

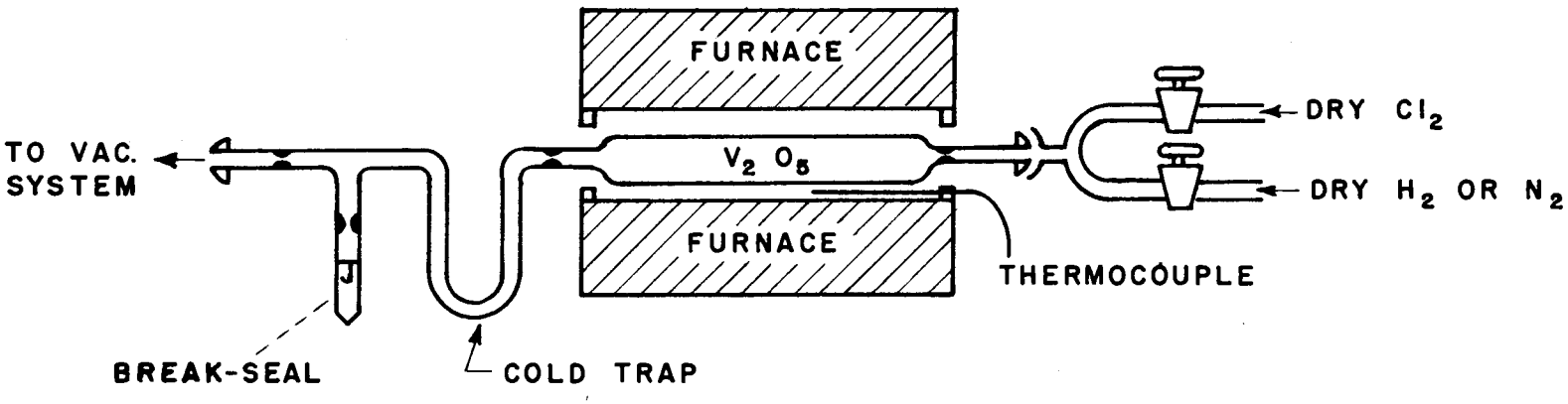

FIGURE I ENHANCED CONVERSION APPARATUS

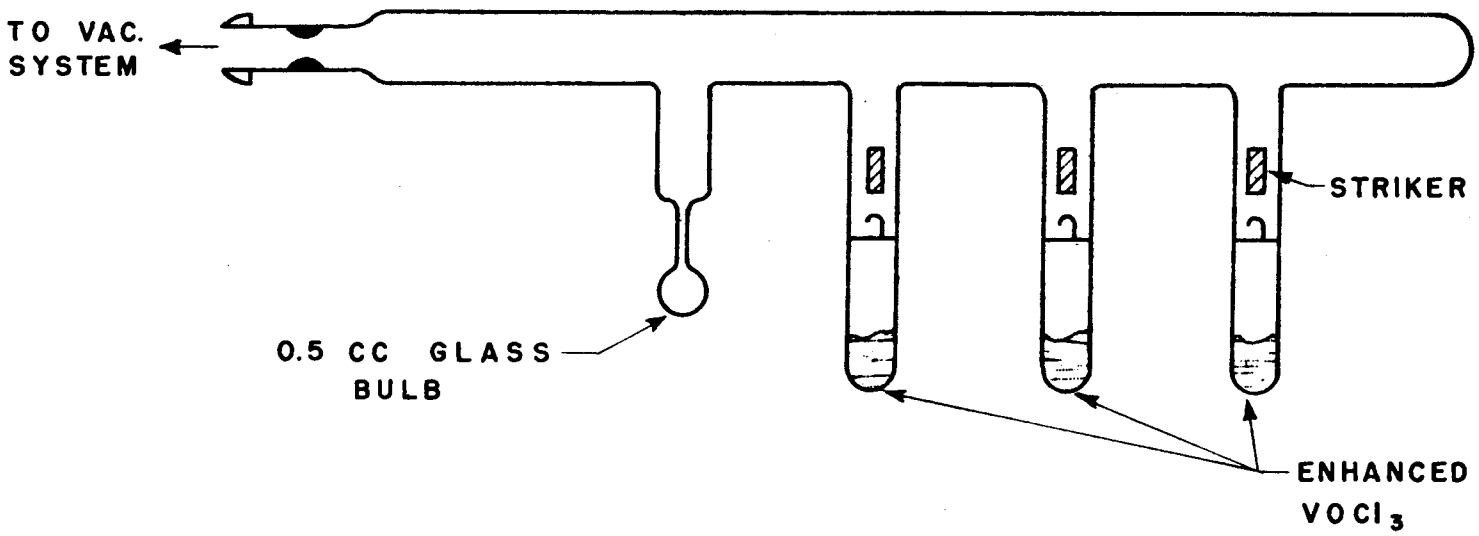

FIGURE 2 COMBINATION APPARATUS

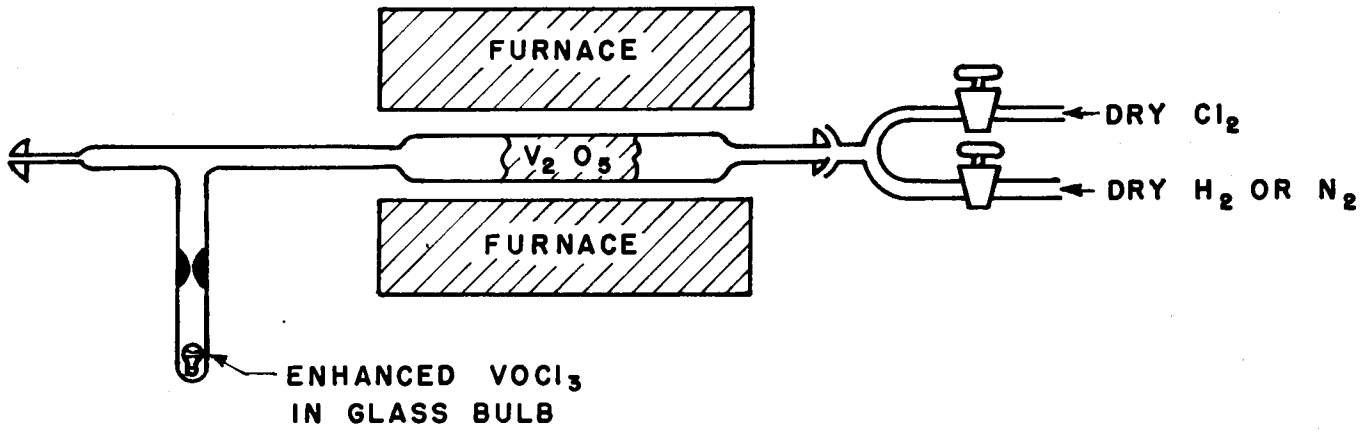

FIGURE 3 NORMAL CONVERSION APPARATUS

Results of a spectrographic analysis which was run on the enriched V_2O_5 showed the following elements present before conversion:

Impurity	Concentration
Cu	0.02 per cent
Fe	0.08
K	0.04
Mg	0.01
Na	0.6
Si	0.08
Ti	0.08

FREQUENCY RATIO DETERMINATIONS

The nuclear gyromagnetic ratio of vanadium 50 was determined in a nuclear induction apparatus similar to that described by Proctor[12] and previously reported.[13] An electronically regulated electromagnet with a gap of 1-3/4 inches produced a field homogeneous to 0.1 gauss over the sample volume. Frequency measurements were made with a Signal Corps BC-221 frequency meter calibrated with harmonics from an external 100 kc, crystal-controlled oscillator, which in turn was compared with radio station WWV at 10 mc.

The sample consisted of 271 mg of electromagnetically enriched vanadium as $VOCl_3$, of which an estimated 25 mg was vanadium 50. This enriched sample was prepared from V_2O_5 as previously described and was sealed in a small spherical glass vial which was placed in a test tube and surrounded by a saturated solution of RbCl containing 15 per cent deuterium oxide (D_2O). No magnetic catalyst was added (Fig. 4).

The vanadium 50 resonance was first observed near 6 mc at a field of 14,250 gauss. Frequency measurements were made at nominal fields of 14,250, 11,900, and 10,100 gauss. The frequency ratios for V50 relative to Cl35, Rb85, and deuterium gave:

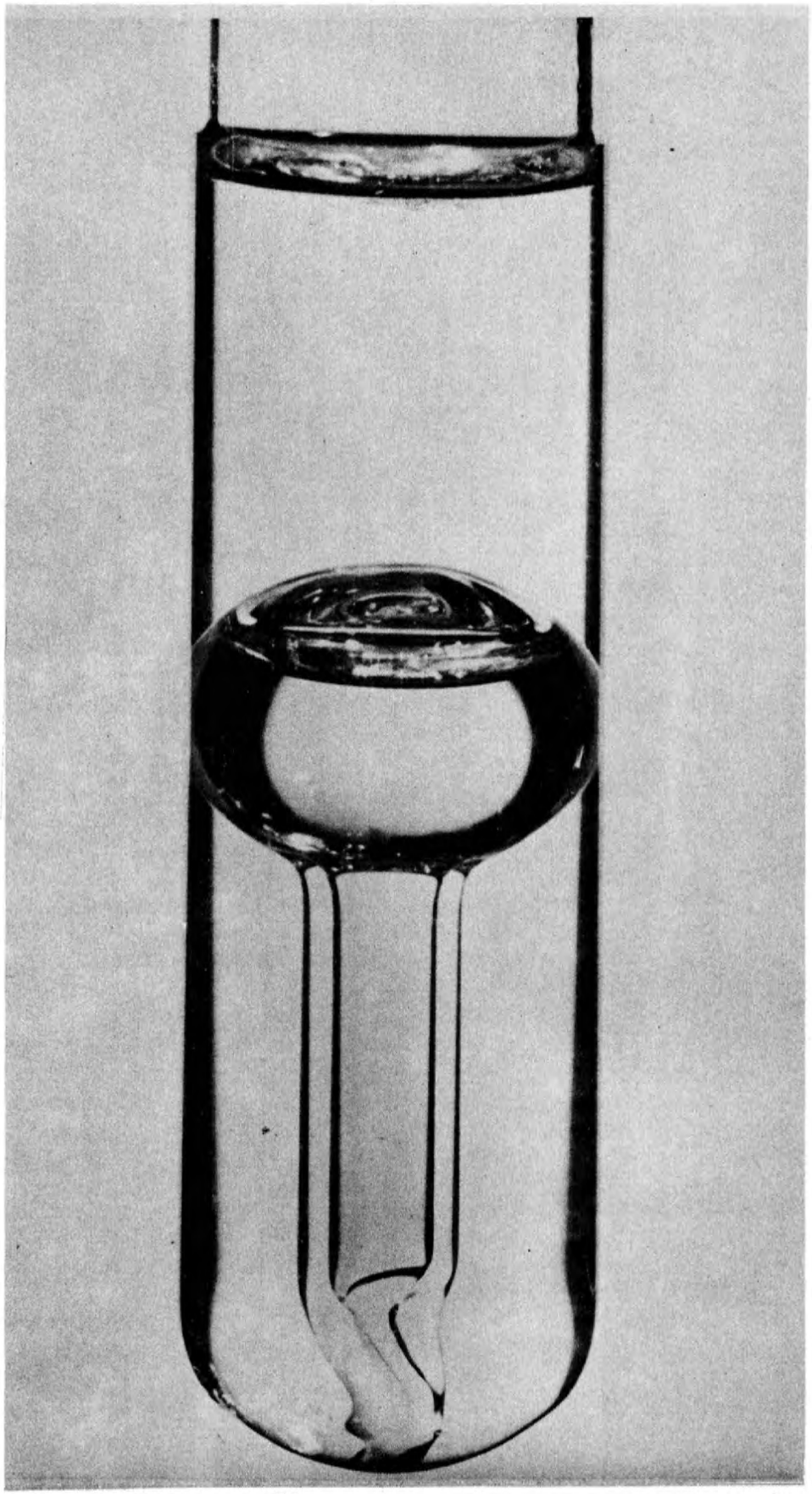

FIGURE 4 ENRICHED $V^{50}OCl_3$ IN AQUEOUS RbCl SOLUTION

		P. E.
$\nu(V50)/\nu(Cl35)$	$= 1.01758 \pm 0.0001$	0.000010
$\nu(V50)/\nu(Rb85)$	$= 1.03262 \pm 0.0001$	0.000028
$\nu(V50)/\nu(D)$	$= 0.649527 \pm 0.00007$	0.000012

Each of the above ratios is the average of three sets having six or more ratio determinations per set. The stated statistical probable error is the greatest probable error found in any of the three sets.

The sign of the moment of V50 has been determined to be positive by direct comparison with Rb85 and Cl35 resonances (see Fig. 5). The improvement in signal amplitude gained by using the enriched sample of V50 can be seen by comparing the resonance trace in Fig. 5 with that of Fig. 6 which was taken using a 5 ml sample of normal $VOCl_3$. The observed line widths for V50, Rb85, and D at 10,100 gauss were 1.75, 2.1, and 0.92 gauss, respectively. Using the uncorrected value of 2.79268 ± 0.00006 n.m.[14] for the proton moment, and E. C. Levinthal's[15] value for the deuteron-to-proton frequency ratio, and a spin of 1/2 for the proton, the nuclear gyromagnetic ratio for vanadium 50 (without diamagnetic correction) becomes $+0.55690 \pm 0.00006$.

The Mayer shell model[16] predicts both odd nucleons to be in $^2F_{7/2}$ states. If the spins are assumed to be additive, the computed nuclear magnetic moment (uncorrected) becomes 3.8983 n.m. Using a diamagnetic correction of 0.171 per cent[21] the corrected value becomes $\mu(V50) = +3.9050$ n.m. which may be compared to the j-j coupling value of 3.85 n.m. as computed from data given by Feenberg.[22]

The vanadium 50 resonance signal was looked for in normal V_2O_5, but none was seen. It is therefore not possible to state that a chemical shift occurs in the $V^{50}OCl_3$. However, a check made for a shift in the resonance of V51 in V_2O_5, $VOCl_3$, and NH_3VO_3 indicated a shift of approximately 0.05 per cent in the direction of a higher field for the $VOCl_3$ resonance.[23] Any such probable shift in the V50 will have to be considered in determining the true gyromagnetic ratio. Further measurements with the V50 sample will be made at a later date.

Frequency measurements were made at the same nominal fields for Rb85, Cl35, and D. The ratios measured with deuterium were converted to those relative to the proton by using E. C. Levinthal's[15] deuteron-to-proton frequency ratio of 0.1535059. Our results are compared with other published values in Table I and Fig. 7.

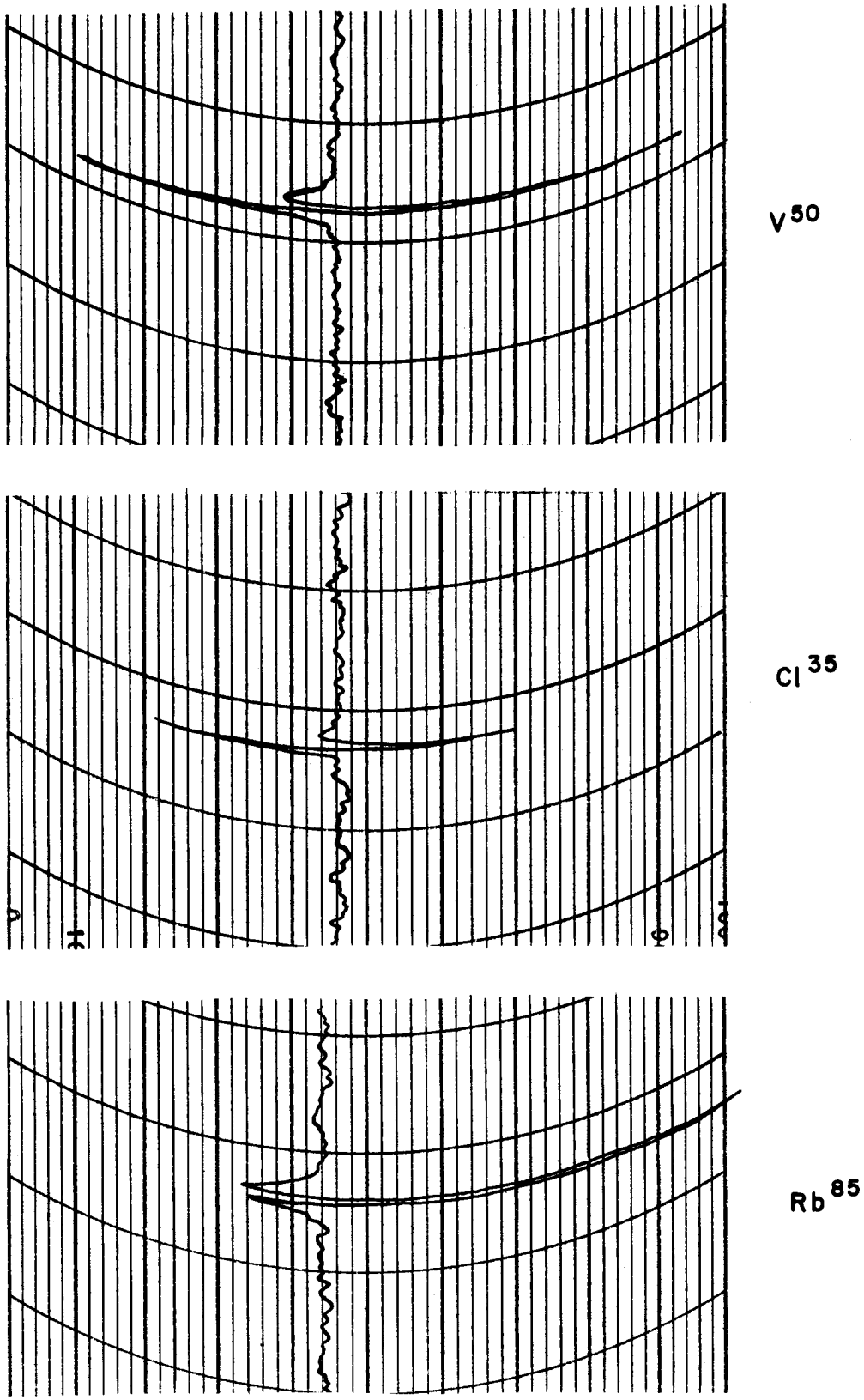

FIGURE 5 RECORDER TRACES

NUCLEAR RESONANCE

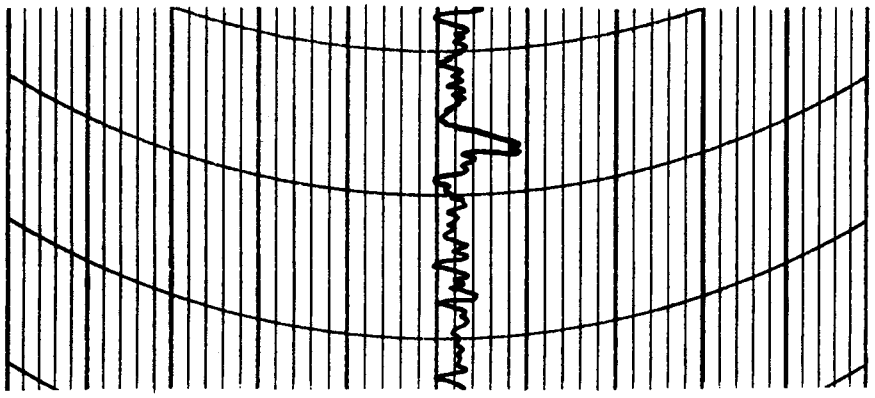

FIGURE 6 THE RECORDER TRACE OF V^{50} RESONANCE IN 5 ml. OF NORMAL $VOCl_3$

TABLE I

COMPARISON OF FREQUENCY RATIO MEASUREMENTS

		Frequency Ratio	Method	Reference
ν(Rb85)/ν(Cl35)	=	0.98545 ± 0.00042	(Rb/Na)(Na/Cl)	Bitter(17)
		0.98592 ± 0.0008	(Rb/H)(H/Cl)	Chambers and Williams(18)
		0.98541 ± 0.00015	Direct	This report
ν(Rb85)/ν(H1)	=	0.096574 ± 0.00004	(Rb/Na)(Na/H)	Bitter(17)
		0.09661 ± 0.00004	Direct	Chambers and Williams(18)
		0.0965521 ± 0.0000003	Direct	Yasaitas and Smaller(19)
		0.096554 ± 0.00001	(Rb/D)(D/H) [15]	This report
ν(Cl35)/ν(H1)	=	0.097999 ± 0.00005	(Cl/Na)(Na/H)	Bitter(17)
		0.09799 ± 0.00007	Direct	Chambers and Williams(18)
		0.097978 ± 0.00009	Direct	Proctor and Yu(20)
		0.097985 ± 0.00001	(Cl/D)(D/H) [15]	This report

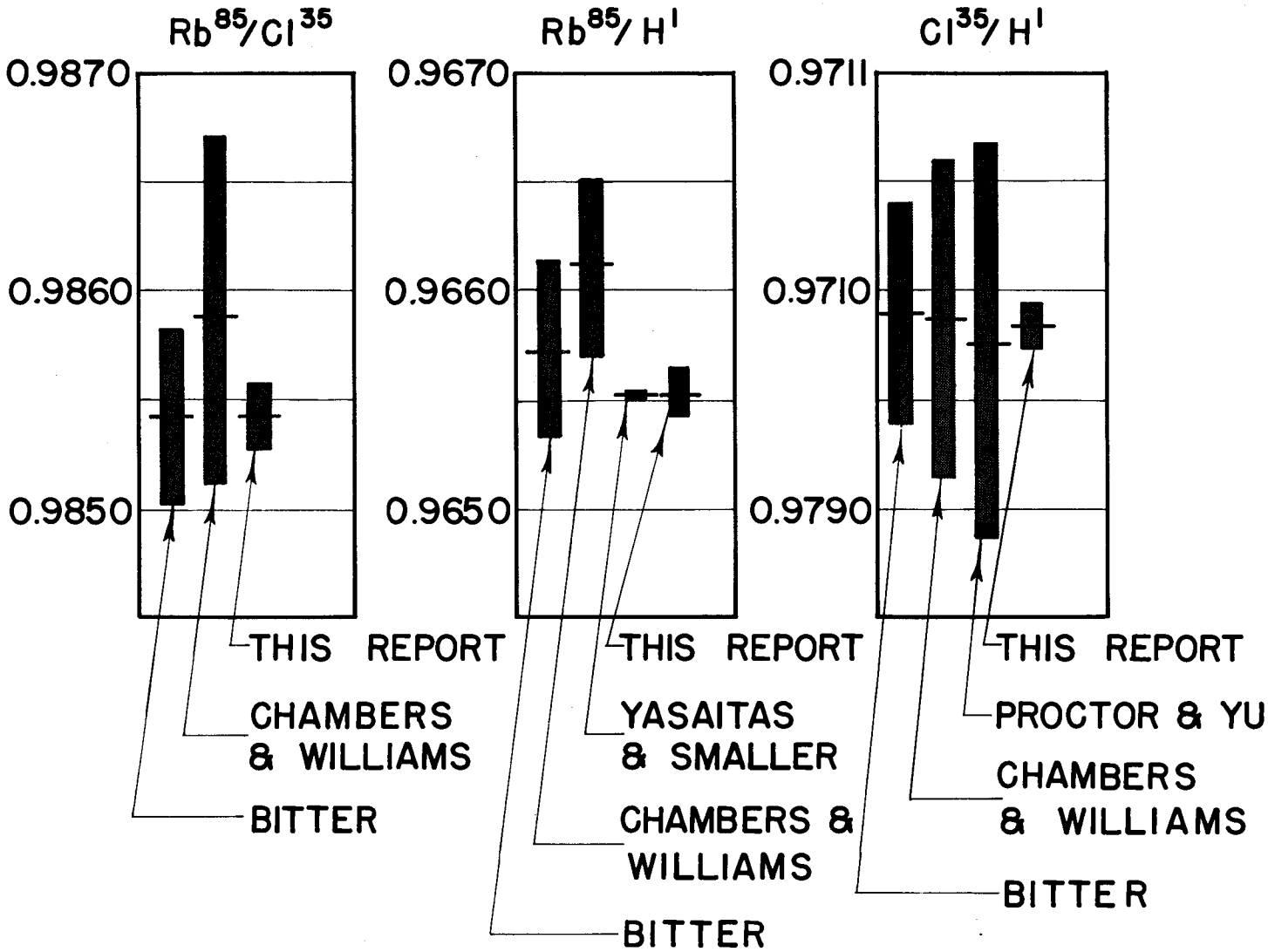

FIGURE 7. COMPARISON OF REPORTED FREQUENCY RATIOS

ACKNOWLEDGMENTS

The authors wish to express their gratitude to J. R. McNally, Jr., H. W. Morgan and other associates for interest and encouragement in this work. Appreciation is also expressed to personnel of the Stable Isotope Research and Production Division who were responsible for the enrichment of the vanadium, its subsequent chemical purification, and the spectrographic analysis.

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